THE FAR ULTRAVIOLET PHOTOLYSIS OF NITRIC OXIDE

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Nitric oxide has been photolyzed in the region 1550-1650A using a hydrogen discharge and at 1470A and 1236A using xenon and krypton discharges respectively. The products at all wavelengths are N_2 and NO_2. At 1470A small amounts of N_2O are produced. The quantum yield of N_2 increases over the nitric oxide pressure range 5-900 mm from ~ 0.2 - 0.5 and also with added inert gas. Quantum yields of NO_2 production and of NO decomposition increase in a similar manner, and the wavelength has no profound effect. Since 1236A light ionizes NO it is concluded that the recombination of NO^+ and an electron leads to an excited molecule which decomposes, as it does at 1600A and at 1470A, into N and O atoms. These react with excess NO producing N_2 and NO_2.

Introduction

The photolysis of nitric oxide has been reported in several papers but there remains doubt about the nature of the products and their quantum yields. In an early study by Macdonald[1] using radiation from an aluminum spark, centered

1 J. Y. Macdonald, J. Chem. Soc., 1, (1928).

around 1900A, nitric oxide was photolyzed at pressures from 50 to 650 mm. The products analyzed by a fractional distillation technique, included nitrogen, nitrogen dioxide, and nitrous oxide in about ten percent of the nitrogen yield. The quantum yield for disappearance of nitric oxide was 1.45, independent of the nitric oxide pressure. The mechanism proposed was:

$$NO + h\nu \rightarrow NO'$$

$$NO + NO' \rightarrow N_2 + O_2$$

$$NO + NO' \rightarrow N_2O + O$$

$$NO + O \rightarrow NO_2$$

It was suggested that the nitrous oxide production might involve reaction of the activated nitric oxide with a nitric oxide dimer; reaction with monomer giving nitrogen and oxygen.

Flory and Johnson[2] in a low pressure study, 0.02 to 7.0 mm.,

2 P. J. Flory and H. L. Johnson, J. Am. Chem. Soc., 57, 2641 (1935).

using radiation from a mercury arc and from sparks between

electrodes of aluminum, zinc, cadmium, nickel, copper and tin, assuming the final products to be nitrogen and oxygen followed the reaction by the rate of pressure change. This rate was found to be directly proportional to the rate of light absorption and, at very low pressures, directly proportional to the pressure. Nitrogen as a diluent was without effect. It was concluded that the dissociation of nitric oxide was the primary step and, by the use of filters, that the effective radiation was below 1900A, probably in the neighborhood of 1830A. Secondary processes considered were wall recombinations of atoms. Flory and Johnson did not consider that nitrous oxide was produced and, without citing evidence, attributed Macdonald's result to analytical error.

The mercury sensitized photolysis was studied by Noyes[3],

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3 W. A. Noyes, Jr., J. Am. Chem. Soc., 53, 514 (1931).

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who found that, after long exposures, the final pressure was one-half of the initial pressure and concluded that nitrogen was the remaining gas. No mercuric oxide was found but rather a mercury salt was formed which could slowly decompose to the oxide. Noyes concluded that a relatively long-lived vibrationally excited nitric oxide molecule was formed in collisions of the second kind with $^3P_1$ or $^3P_0$ mercury atoms and some of these molecules eventually decomposed.

The increased interest in outer space and the chemistry

of the upper atmosphere stimulated work in the far ultraviolet. Marmo[4] measured the absorption coefficients of nitric oxide

4 F. F. Marmo, J. Opt. Soc. Am., 43, 1186 (1953).

in the spectral region 1100-2300A. A continuous absorption was found between 1100 and 1400A with the absorption coefficients varying from about 40 to 200 cm^{-1}. From 1400 to 2300A a highly structured spectrum was obtained, with a weak underlying continuum possible between 1400 and 1500A with a maximum at 1470A. The ionization potential of the oxide was shown by Watanabe[5] to be

5 K. Watanabe, J. Chem. Phys., 22, 1564 (1954).

9.23 E.V. (1343A) and for light of shorter wavelength than about 1250A, the ionization efficiency was complete. Hence for all photons of wavelength less than 1230A

$$NO + h\nu \rightarrow NO^+ + e$$

The ions and electrons would then presumably be removed by dissociative recombination[6] : $NO^+ + e \rightarrow N + O$. Zelikoff

6 a. A. P. Mitra and R. E. Jones, Scientific Report No. 44, Ionosphere Research Laboratory, Pennsylvania State, March 1953.

b. B. E. Squires, Jr., "Cross Section for Dissociative Recombination of Nitric Oxide", thesis Pennsylvania State, 1961.

and Aschenbrand[7] attempted to show experimentally that the

7 M. Zelikoff and L. M. Aschenbrand, J. Chem. Phys., 25, 674 (1956).

dissociative recombination does occur; however, their results simply showed that electrons were produced. By irradiating nitric oxide at pressures between 0.43 and 3.25 mm. with 1236A radiation from a krypton resonance lamp, they observed the current between two electrodes in the reaction vessel. As the voltage across the electrodes was increased from 70 to 300 volts, the measured current and the percentage decomposition increased. They concluded that the acceleration of the ions and electrons by the applied voltage was responsible for the increased decomposition, that absorption of 1236A light by nitric oxide leads only to ionization and that recombination of ion and electron is responsible for the decomposition although the value of the recombination coefficient could not be determined.

Doering and Mahan[8] have recently attempted to determine the

8 J. P. Doering and B. H. Mahan, J. Chem. Phys., 36, 669 (1962).

rate constant for the recombination. Photolyzing nitric oxide with 1236A light at pressures between 0.05 and 0.15 mm., they measured the photostationary ion concentration using a Langmuir probe. They found that the ion concentration depended on the

square root of the rate of ion production, attributing this dependence to the dissociative recombination reaction. However, the same dependence would be found without dissociation so long as the excited nitric oxide molecule formed on recombination did not produce any further ions. In addition to the probe measurements, the rate of decay of the electron concentration in the gas after interruption of the ionizing radiation was measured and gave an average value of 3.2×10^{-7} cc/ion sec. for the recombination rate constant. This is to be compared with the probe measurement value of 2×10^{-6} cc/ion sec.

Tanaka and Steacie[9] using a krypton resonance lamp photolyzed nitric oxide between two electrodes with an applied potential

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9 I. Tanaka and E. W. R. Steacie, J. Chem. Phys., 26, 715 (1957).

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of 22.5 volts and found that the current produced could be increased by the addition of krypton to the nitric oxide. They interpret this as a photosensitization, krypton absorbing its own radiation more strongly than does nitric oxide, the excited krypton ionizing the nitric oxide.

The purpose of the present work was to determine whether a change in the mechanism of nitric oxide decomposition occurred with light above and below the ionizing wavelength. To this end the quantum yields of products were obtained as a function of the initial pressure of nitric oxide and the presence of inert gases

on irradiation with a hydrogen discharge (1550-1650A), a xenon discharge (1470A) and a krypton discharge (1236A).

Experimental

a. Materials

Matheson Co. specially purified nitric oxide showed a contamination by its mass spectrum and was purified by freezing in liquid nitrogen and evacuating the non-condensables. The sample used was distilled off at -160°C using isopentane slush, through two traps cooled with dry-ice-acetone. This procedure was repeated twice. The mass spectrum showed no extraneous peaks.

Airco reagent grade hydrogen, xenon, krypton and argon were used without purification. Matheson Co. prepurified nitrogen and helium were drawn from the tank through two liquid nitrogen traps. Matheson extra dry oxygen was used directly from the tank for the actinometry.

b. Light Sources

1) Hydrogen Lamp. An electrode lamp powered by a luminous sign transformer was constructed from the description given by Comes and Schlag.[10] The light was transmitted into the attached

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10 F. J. Comes and E. W. Schlag, Z. physik. Chem., N. F. 21, 212 (1959).

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reaction vessel through a lithium fluoride window, 20 mm. in diameter and 2 mm thick. The lamp was operated at ~ 2.5 mm

pressure of hydrogen. The light output for a similar, microwave operated, lamp is reported by Warnecke[11] as

11 P. Warnecke, Applied Optics, 1, 721 (1962).

predominantly between 1550 and 1650A, with some Lyman alpha (1215A) present. Two such lamps were used during the course of the work. The first had an output of 1.8×10^{15} quanta per sec.; the second, initially 11×10^{15}, deteriorating with use to 2.0×10^{15} at the end of the work. A double chamber reaction vessel was used with the second lamp, the chambers separated by a lithium fluoride window 45 mm in diameter and 5 mm thick. The ratio of the lamp output determined in the first chamber to that in the second was 8.12.

2) Xenon and Krypton Lamps. The same lamp body was used to generate the xenon and krypton resonance lines depending on the lamp filling. The lamp followed the design given by Schlag and Comes[12] and was operated at ~1 mm pressure using a Baird 12.5 cm

12 E. W. Schlag and F. J. Comes, J. Opt. Soc. Am., 50, 866 (1960).

Microwave Excitor. Care was taken to remove water vapor from the lamp filling. The output of the lamp was between 3.0 and 1.0×10^{15} quanta per sec. for the krypton lines at 1236 and 1165A.

c. Procedure

The photolysis experiments were carried out in a static system. Before being charged with nitric oxide, the reaction vessel was pumped through a liquid nitrogen trap for at least 15 min. to remove mercury vapor. Nitric oxide was admitted, the vessel isolated and the lamp operated for a measured time. Mixtures of gases, when used, were prepared by collecting required amounts of each constituent in separate volumes, then freezing them together or allowing them to diffuse together to form the mixture.

After irradiation the products and unreacted gases were expanded into a series of three traps. For the earlier results with the hydrogen lamp these three traps were cooled with liquid nitrogen and the nitrogen produced in the reaction, along with some nitric oxide was Toepler pumped into the known volume of an octoil manomer. The total moles of gas could be calculated from the pressure, temperature and volume. A sample of this gas was analyzed mass spectrometrically to determine the nitrogen content. In the later experiments, two techniques for the analysis of all products were used. In both methods nitrogen was removed by expanding and Toepler pumping the reaction vessel gases through the three traps, the first and third in liquid nitrogen, the second in solid nitrogen obtained by pumping on liquid nitrogen. The remaining gases, caught in the traps one and two, were vaporized after the nitrogen had been removed and their total amount determined. A known volume of oxygen was then added to oxidize the nitric oxide. At least one hour of warming and cooling was required for anything

close to complete reaction. The residual oxygen was Toepler pumped into a known volume. From the loss of oxygen, the amount of nitric oxide present could be calculated and, if no nitrous oxide was present, the remaining sample was taken as nitrogen dioxide. In an analysis for nitrous oxide, the mixture of N_2O_4 and N_2O was cooled with pentane slush at -130°C or carbon disulfide slush at -110°C to freeze out the N_2O_4. The volatile nitrous oxide could than be removed and measured. This scheme permitted an analysis of all products including unreacted nitric oxide; however the reaction with oxygen was quite slow and seemed never quite complete.

A second technique was faster and was used for most of the experiments. After removing the nitrogen at -210°C, the coolants on the traps were removed and traps one and three were cooled to -160°C. Volatile nitric oxide was pumped off and the amount determined. Nitrous oxide could next be removed by changing the temperature of the traps to -130°C. The residue in trap one was N_2O_3 formed on condensation of NO and NO_2 when NO was in excess. The analysis for NO_2 was accomplished by volatilizing the N_2O_3 and determining its amount. It was assumed that one half of this was NO and one half, NO_2. The assumption is reasonable since the total pressure was low and the decomposition of N_2O_3 and N_2O_4 would be almost complete. From the data of Verhoek and Daniels[13] the

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13 F. H. Verhoek and F. Daniels, J. Am. Chem. Soc., 53, 1250(1931).

maximum error to be expected for the incomplete dissociation of these gases is 0.9 percent for a total pressure of 7 mm at 25°C. Actually the results would be better since the pressure was generally lower and the temperature higher.

Two problems were encountered in the NO_2 determination which tended to reduce the observed quantum yield. The first was the presence of mercury since it could react with NO_2 to give a non-volatile product. This was obviated by the initial pumping through liquid nitrogen to remove mercury and the use of the octoil manometer. The second problem was more serious and was encountered when N_2O_3 was volatilized and recondensed without excess NO present. Instead of N_2O_3 being recondensed, N_2O_3 and N_2O_4 were condensed at -160°C, some NO remaining in the gas phase. This error was eliminated by keeping N_2O_3 frozen at all times until the last step. The analysis scheme was checked by collecting the respective fractions and analyzing them using a mass spectrometer.

The output of the lamps was measured by flowing oxygen through the reaction vessel at atmospheric pressure at ~ 200 ml per min. The ozone produced was trapped in a neutral KI solution and the iodine formed was titrated with standard thiosulfate solution. The quantum yield of ozone formation was taken as 2.0.[14,15] In

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14 W. Groth, Z. physik. Chem., B37, 307 (1937).

15 W. A. Noyes,Jr., J. Am. Chem. Soc., 52, 559 (1930).

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many of the experiments the lamp output was determined both before

and after the photolysis run. It was found, however, that a determination after the photolysis was sufficient.

Results

Hydrogen Discharge Table I presents results with the first lamp used and only quantum yields of N_2 production were obtained. Table II shows data with the second lamp, as quantum yields of N_2 and of NO_2 production as well as of NO decomposition. The yields of NO_2 produced and NO decomposed are in error in all cases except in runs 55,56,86,89 and 91 since either mercury was not removed, or N_2O_3 was allowed to volatilize and recondense. No concrete evidence for the production of N_2O could be obtained in this spectral region, either from pure NO or when helium argon or nitrogen was added.

[Tables I and II]

Xenon and Krypton Discharge The results obtained with the xenon and krypton discharge lamps are shown in Tables III and IV respectively. The quantum yields obtained with both these lamps parallel each other and are generally higher than the yields with the hydrogen lamp. The products are still N_2 and NO_2, but with the xenon lamp small amounts of N_2O are produced. The determination of this small amount of N_2O is difficult since the fractionation technique may have permitted some N_2O_3 to have been measured together with the N_2O. Mass spectromatic analysis, too, is uncertain, since when NO_2 is present, oxidation of carbon on the filament yields CO_2 with a mass peak at 44.[16] The amount

16 R. A. Friedel, A. G. Sharkey,Jr., J. L. Shultz and C. R. Humbert, Anal. Chem., 25, 1314 (1953).

of CO_2 must be judged from the small mass peak at 22 which is not present with N_2O. Resultantly the most reliable estimate of the N_2O quantum yield is about 0.02, far less than the maximum values listed in Table III. The quantum yields of NO decomposition, since the amount of NO decomposed is obtained as the small difference of two large numbers, are not expected to be very accurate.

[Tables III and IV]

Discussion

The experimental results can be discussed in the light of the following scheme:

1. $NO + h\nu \rightarrow NO^*$
2. $NO^* + M \rightarrow N + O + M$
3. $NO^* \rightarrow NO$ (+ $h\nu'$ or radiationless transition)
4. $NO^* + M \rightarrow NO + M$
5. $N + NO \rightarrow N_2 + O$
6. $O + NO \rightarrow NO_2$

With the krypton lamp the following additional reactions are necessary:

7. $NO + h\nu \rightarrow NO^+ + e$
8. $NO + e \rightarrow NO^*$

The asterisk in all cases indicates an electronically excited state of the NO molecule. Wall recombinations of nitrogen atoms and of oxygen atoms may be possible at very low pressure but in the current work at 5 to 900 mm they are unlikely. The homogeneous recombination of nitrogen atoms could give a quantum yield of o.5 for N_2 production as observed. Kistiakowsky and Volpi[17], however, have shown that reaction 5 as well as 6 is very

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17 G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys., 27, 1141 (1957).

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fast. Since the quantum yields of N_2 and NO_2, and the quantum yield of NO decomposition all rise with an increase in the initial pressure of NO, and with added inert gas, the inclusion of reactions 3 and 4 is necessary. Furthermore, since the quantum yield of nitrogen levels off at about 0.5 when the xenon and krypton lamps are used, then $k_2[M] \simeq k_3 + k_4[M]$ for these spectral regions. With the hydrogen lamp the yield of N_2 levels off at about 0.4 and $k_2[M] < (k_3 + k_4[M])$. The spectral region, 1550-1650A, of the hydrogen lamp lies in a strongly banded region of the nitric oxide spectrum and it would appear likely that deactivation might be more marked than at 1470A or 1236A.

The dissociative recombination reaction:

9. $$NO^+ + e \rightarrow N + O$$

has been predicted theoretically[6], although no experimental

proof has really been offered for this reaction. The similarity of the results in the present experiments with both xenon and krypton radiation would seem to indicate that reaction 9 does not occur. The limiting values at high pressures of the quantum yields of N_2 and NO_2 are about 0.5 and 1.0 respectively. If reaction 9 occurred, followed by reaction 5, the quantum yield of N_2 would be 1.0, independent of pressure. Since it has been shown that 1286A radiation leads to complete ionization, it does not seem reasonable that a fortuitous combination of reactions 2 and 9 producing the same quantum yields at 1236A as at 1470A could be responsible. It is much more reasonable to assume that the recombination of an NO^+ ion and an electron produces an excited state of NO that is similar to the state formed with 1470A light of the xenon discharge.

The one difference between the results at 1470A and at 1236A is the formation of nitrous oxide with the xenon light. Kistiakowsky and Volpi[17] studied the reaction of nitrogen atoms with NO_2 indicating that N_2O was produced. Again there was difficulty with the analysis and conceivably some of the N_2O reported may have been CO_2 formed through oxidation by NO_2 of carbon in the filament of the ion source of the mass spectrometer. However, in one experiment reported, the mass spectrometer, which was connected to their reaction vessel, was conditioned with NO_2 for a relatively long time, yet, N_2O was still produced and

it was concluded that the reaction:

$$10. \quad N + NO_2 \rightarrow N_2O + O$$

occurs and that it is quite fast.

In the present experiments with the hydrogen lamp no N_2O was detected. The reaction vessel was larger in volume than that used with the xenon lamp. As a result, the partial pressure of NO_2 always remained small during the photolysis. In addition, the absorption coefficient of NO is smaller in the region 1550-1650A than at 1470A, permitting the photo-reaction and consequent NO_2 production to be spread more uniformly over the length of the reaction vessel. The xenon and krypton experiments used the same reaction vessel and the only apparent reason that N_2O was not detected at 1236A must be the lower intensity of the krypton lamp, the consequent smaller amounts of product reducing the secondary reactions of NO_2. The absence of N_2O reported by Flory and Johnson[2] is consistent with the inclusion of reaction 10 in the present scheme, since they removed NO_2 as the photo-reaction progressed. Conditions in the current study were more nearly similar to those of Macdonald[1]; however, there is a discrepancy between his finding 10 percent of the reaction producing N_2O and the very small yield reported here. The problem of the production of N_2O is being studied further.

Table I

Photolysis of Nitric Oxide

Hydrogen Discharge; Early Results with first lamp.

Run No.	Initial NO mm Hg.	Added Gas Gas	Added Gas P in mm	% NO	ϕN_2	N_2O
14	55.2				0.415	
15	124.4				0.466	
4	181.0				0.520	None
18	181.2				0.511	
6	186.2				0.581	
19	280.5				0.489	
7	285.4				0.590	
17	737.9				0.486	
16	756.6				0.535	
29	812.9				0.542	
20	33.8	Ar	43.5	43.72	0.565	
28	38.4	Ar	49.8	43.55	-	None
32	161.7	N_2	202.1	44.44	-	None

Table II

Photolysis of Nitric Oxide

Hydrogen Discharge. New Lamp

Run No.	Initial NO mm Hg	Added Gas Gas	Added Gas P mm	Added Gas % NO	ϕN_2	ϕNO_2	ϕNO	N_2O	$\phi NO_2/\phi N_2$	$\phi NO/\phi N_2$
60	1.539				0.215	0.333	0.812		1.55	3.78
49	4.858				0.268	0.403	1.117		1.50	4.17
56	5.202				0.326	0.666	1.314		2.04	4.03
54	5.389				0.410					
55	5.651				0.333	0.607	1.285		1.82	3.86
57	6.499				0.254	0.301	0.931		1.22	3.67
58	7.278				0.238	0.338	0.958		1.42	4.03
37	10.11				0.399					
64	15.05				0.235	0.312	0.913		1.33	3.89
53	15.61				0.330					
33	22.40				0.326					
59	32.12				0.299	0.420	1.198	None	1.40	4.01
66	37.60				0.310	0.453	1.311	None	1.46	4.23
68	38.66				0.273	0.452	1.326		1.66	4.86
63	39.44				0.296	0.501	1.322		1.69	4.47
51	149.0				0.410	0.732			1.79	
45	167.0				0.388		1.786			4.60
86	205.4				0.418	0.851		None	2.04	
69	341.2				0.412	0.700			1.70	
70	480.2				0.403	0.631			1.57	
39	495.8				0.433	0.735			1.70	
62	6.989	N_2	184.0	3.66		0.336	0.829			
61	7.009	Ar	195.0	3.46		0.331	0.827	None		
89	167.7	Ar	259.1	39.26		0.986	1.422			

Table III

Photolysis of Nitric Oxide

Xenon Discharge

Run	Initial	Added Gas								
No.	NO mm	Gas	Pmm	%NO	ϕN_2	ϕNO_2	ϕNO	ϕN_2O Max.	$\phi NO_2/\phi N_2$	$\phi NO/\phi N_2$
35	10.11				0.353					
82	26.00				0.292	0.624	1.329	0.12	2.14	4.55
78	104.9				0.417	0.839		0.12	2.01	
12	107.3				0.455					
79	119.4				0.415	0.807		0.055	1.94	
80	209.5				0.466	0.913		0.097	1.96	
76	344.2				0.523	1.019	2.709	0.053	1.95	5.18
77	364.6				0.537	1.065	2.538	0.022	1.98	4.73
41	495.8				0.543					
81	701.9				0.534	1.083	2.483	0.11	2.03	4.65
26	69.45	Ar	75.11	48.0%	0.568					

Table IV

Photolysis of Nitric Oxide

Krypton Discharge

Run No.	Initial NO mm	Added Gas			ϕN_2	ϕNO_2	ϕNO	N_2O	$\phi NO_2/\phi N_2$	$\phi NO/\phi N_2$
		Gas	P mm	%NO						
74	9.623				0.227	0.458	1.004		2.02	4.42
65	37.61				0.402	0.622	1.757	None	1.55	4.37
67	38.66				0.399	0.605	1.907		1.52	4.78
87	205.4				0.463	0.765	2.294	None	1.65	4.95
71	304.9				0.510	0.987	1.495		1.94	2.93
75	375.7				0.466	0.910	1.877		1.95	4.03
72	953.1				0.521	1.051			2.02	
73	10.24	N_2	53.34	16.11		0.336	0.814			
88	158.4	Ar	384.6	29.06		1.194		None		
90	167.7	Ar	111.8	58.82		1.055				
85	10.45	Xe	48.52	17.70	0.340					
95	25.99	Kr	13.01	66.67		0.627		None		